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Characterization of Vanadium Flow Battery

Risø-R-Report

Henrik Bindner, Claus Ekman, Oliver Gehrke, Fridrik Isleifsson
Risø-R-1753(EN)
October 2010

Risø DTU
National Laboratory for Sustainable Energy

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Title: Characterization of Vanadium Flow Battery
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Risø-R-1753(EN)
October 2010

Abstract (max. 2000 char.): This report summarizes the work done at Risø-DTU testing a vanadium flow battery as part of the project "Characterisation of Vanadium Batteries" (ForskEl project 6555) with the partners PA Energy A/S and OI Electric A/S under the Danish PSO energy research program. A 15kW/120kWh vanadium battery has been installed as part of the distributed energy systems experimental facility, SYSLAB, at Risø DTU. A test programme has been carried out to get hands-on experience with the technology, to characterize the battery from a power system point of view and to assess it with respect to integration of wind energy in the Danish power system.

The battery has been in operation for 18 months. During time of operation the battery has not shown signs of degradation of performance. It has a round-trip efficiency at full load of approximately 60% (depending on temperature and SOC). The sources of the losses are power conversion in cell stacks/electrolyte, power converter, and auxiliary power consumption from pumps and controller.

The response time for the battery is limited at 20kW/s by the ramp rate of the power converter. The battery can thus provide power and frequency support for the power system.

Vanadium battery is a potential technology for storage based services to the power system provided investment and O&M cost are low enough and long term operation is documented.

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Preface

This report summarizes the work done at Risø-DTU testing a vanadium flow battery as part of the project "Characterisation of Vanadium Batteries" (ForskEl project 6555) under the Danish PSO energy research program. Project partners are Risø DTU, PA Energy A/S and OI Electric A/S. The goal of the Danish TSO Energinet.dk has been to get hands-on experience with the technology and evaluate its potential role in the future Danish energy system. In order to reach this goal a vanadium battery has been acquired and installed at the distributed energy research facility SYSLAB at Risø-DTU. The control and data logging system of SYSLAB has made it possible to carry out a variety of tests of the battery system, thereby gaining understanding of the performance and experience with the integration of the technology in a renewable dominated energy system. This report presents the results of the analyses carried out during 2008 and 2009.

1 Introduction

1.1. Background for project

In the development towards a more sustainable power system the level of renewable energy, in particular wind and solar, is reaching levels were it has a very significant impact on the operation of the system due to the fluctuations in the production and the limited predictability. Since the power system has to be balanced at all time instances the fluctuations coming from the RE has to compensated for by the rest of the system either the production, the consumption or using energy storage. Increasing amounts of RE also implies reduced production from conventional sources and there is thus a desire to shut down these plants but they are often required to be online because of their capability to participate in the control of the system. This indicates that the case for energy storage including batteries is becoming increasingly more attractive.

Many types of energy storage exist ranging from ultra capacitors to large pumped hydro installations. Electrochemical batteries have many attractive features in a power system context for applications in the minutes to hour timescale. These features include power and energy densities, response time and efficiencies that make them suitable for utility applications.

One of these technologies is the all vanadium redox flow battery investigated in the present project.

1.2. Outline of project

The objective of the project is to characterize a vanadium battery from a power system point of view, in particular with respect to applications related to integration of wind energy.

The project has involved procurement and installation of a 15kW/120kWh vanadium battery. It has been integrated as part the the test facility for distributed power systems, SYSLAB, at Risø DTU. A number of tests has been conducted to carry out a characterization of the battery in a power system context. Emphasis has been on getting real hands-on experience and quantifying performance measures in particular the efficiency under different operating conditions.

The objective of the project is to contribute to establish a foundation for decisions on future development and demonstration activities involving vanadium batteries in the Danish power system with respect to large scale application. This will be achieved through measurements on a prototype in order to

- Obtain first hand operating experience with a vanadium battery
- Establish system characteristics of the vanadium battery based on application in the Danish power system including comparison with expected performance characteristics
- Assess the development perspectives of the technology
- Enumerate possible applications and assess the suitability of the vanadium battery for these applications
- Compare with alternative technologies such as other types of batteries, compressed air etc.

1.3. Introduction to Vanadium Flow Battery Technology

Vanadium battery technology is based on electron/H^+ transfer between different ionic forms of vanadium. The battery consists of two closed electrolyte circuits and the liquid electrolytes containing the vanadium ions flow from two separate containers for each half cell through an electrochemical cell on each side of the membrane and back to the container. The electrochemical potential over the cell is used to convert the chemical energy to electrical energy (in the discharge mode) or vice versa (in the charge mode). The chemical reactions are:

Positive electrolyte:

$$VO_2^{+} + e^{-} + 2H^{+} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} VO^{2+} + H_2O$$

Negative electrolyte:

$$V^{3+} + e^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}$$

The standard voltage over one cell is around 1.4V and cells are therefore stacked in order to reach higher voltages. Figure 1shows a schematic drawing of the battery technology. Note, that the electrolyte does not flow between the electrolyte tanks - the pumps make the electrolyte flow through each of the half cells back to the same tank, ensuring that there at all times is sufficient electrolyte in the cells willing to undergo the chemical reactions.

The concept is different from conventional batteries where the electrodes take part in the chemical reaction. The chemical reduction/oxidation and the flow of electrolyte (which facilitates the electron transfer and therefore the energy storage) have caused the name: (vanadium) redox flow battery. More details on the technology can be found in ref. [1].

A number of technology advantages are often highlighted:

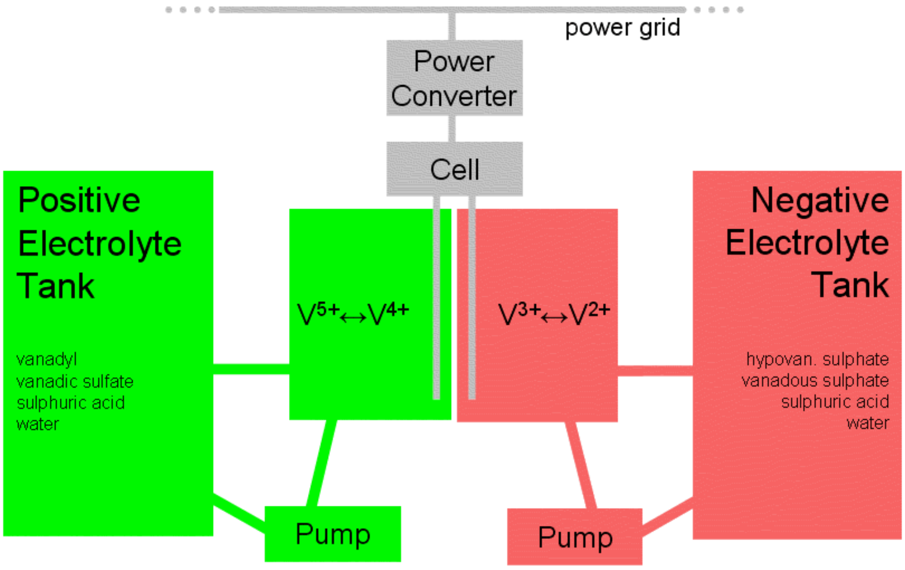

Figure 1 Schematic drawing of a vanadium battery. The aqueous electrolyte is pumped into the fuel cells (here only one cell is depicted) on each side of the cell membrane. The concentration of the different vanadium ions in the two electrolytes leads to an electrochemical potential over the cells.

- Power and storage capacity can be sized independently by adding more cell stacks or more electrolyte solution.
- The technology is responding very fast (<100μs). The response time is limited by the electronics rather than the electrochemistry. This makes the technology suitable for frequency and voltage support.
- The system life time is claimed to be long. The electrolytes should in principle not get degraded, while it is expected that the cell stacks should be replaced every 10 years.
- The technology has a relatively high efficiency. The large open circuit voltage and the relative small ohmic resistance make the electrochemical part of the system very efficient. The overall efficiency is lower (~60% round trip), due to losses in the power electronics and auxiliary components.
- The self discharge is very low, since the electrolytes are physically separated.

- The technology offers the possibility of overloading the cell stacks - up to twice the rated power for minutes (this has not been verified or tested in the studies presented in this report).

However, there are also a number of disadvantages:

- The energy density of the storage system is relatively low (~0.02MWh/m^3), comparable to natural gas at atmospheric pressure. This makes the footprint of a vanadium battery large.
- The large quantity of electrolyte consists of sulphuric acid and is thus classified as corrosive. Measures have to taken to avoid leakage to the environment.
- The technology is (still) relatively expensive – both in terms of price per unit of power (cell stacks) and price per unit of electricity storage (electrolyte). In particular the cost reduction potential of the electrolyte is limited due to the high dependency on the cost of vanadium.

2 Experimental Setup and Operation

The vanadium battery is installed at Risø as part of SYSLAB. SYSLAB (www.syslab.dk) is a research platform for distributed intelligent energy systems with a high penetration of renewable energy. It can be used for testing of components including characterization, control of components as part of a larger system and investigating system control concepts such as decentralized control or large scale participation of the demand side in system balancing. SYSLAB is very flexible both with respect to configuration of the system under study and with respect to control.

2.1. The experimental facility SYSLAB

SYSLAB is a distributed platform for research in distributed power systems based on real energy sources. SYSLAB consists of three interconnected sites, Figure 2. It includes two wind turbines (11kW and 55kW), a PV-plant (7kW), a diesel genset (48kW/60kVA), an intelligent office building with controllable loads (20kW), and a number of loads (75kW, 3*36kW). At each of the three sites there is a switchboard that allows the components installed at the site to be connected to either of two bus bars. The two bus bars at each site are connected to a crossbar switchboard allowing the flexible setup of the system(s) to be studied. The bus bars can be either connected to the national grid or can be part of an isolated system. It allows components and systems to be in grid connected operation, island operation, or operation in parallel with wind turbine or PV-plant. The components are all connected in one distributed control and measurement system that enables very flexible setup with respect to experimental configuration.

The control platform provides infrastructure for control of the components as well as for

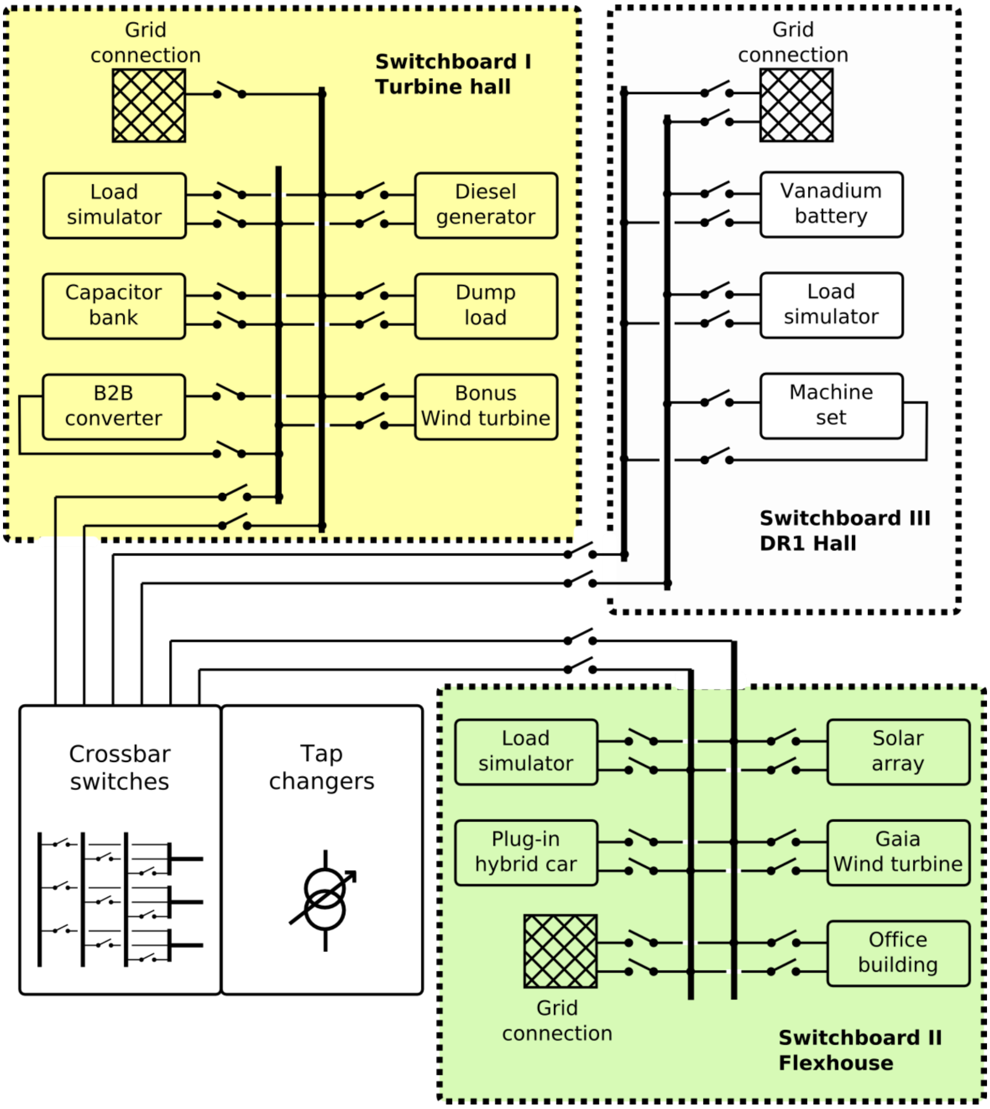

Figure 2 Layout of power part of SYSLAB. The three sites each have a two bus bar switchboard that can be either connected to the main grid or through the crossbar switchboard to the other sites.

groups of components or systems. It makes it possible to program complex control sequences that can be automatically executed as well as to program control algorithms to investigate the performance of components as part of a system e.g. as a virtual power plant or parallel operation of wind turbine and battery with the objective of firming the wind power.

SYSLAB also provides an infrastructure for measurements. It includes measurement devices installed in the switchboards and signals from the system components incl. the battery control system. It can also provide signals from other parts of the system that can be used in control algorithms.

2.2. The Vanadium Battery in SYSLAB

The vanadium battery system installed in SYSLAB is connected to the grid via a four quadrant power converter and can deliver ±15kW on the AC side and the nominal storage capacity is 120kWh. Figure 3 shows a picture of the system during installation and list the main system components. The battery can operate in two modes: P-Q mode (where the active and reactive power of the battery is set by the user) and U-f-mode where the power is set according to the grid voltage and frequency and the pre-defined droop-curves.

System components:

- Cell stacks (3×40 cells in total)
- Electrolyte tanks (2×6500 liter)
- Balance of plant (pipes, pumps, etc.)
- Control and communication unit
- AC/DC power converter

Figure 3: Photograph of the vanadium battery at SYSLAB during installation. To the right, the system components are listed.

The current installation is shown in Figure 4. The area of the installation is 7m x 7m.

Figure 4Vanadium battery installation seen from above: electrolyte tanks in the back, 3 cell stacks at the front.

2.3. Communication and data acquisition

The battery is fully integrated in SYSLAB. The control of the battery is via modbus interface between the battery controller and the SYSLAB node. The interface allows start/stop and error resetting of the battery as well as access to a number of internal measurement values including electrolyte temperatures and measurement cell voltage. Further are the active and reactive power flow measurements of the power converter as well as of the auxiliary power consumption measured using panel instruments in the associated switchboards. The measurement setup is shown in Figure 5. Data is sampled at 1Hz.

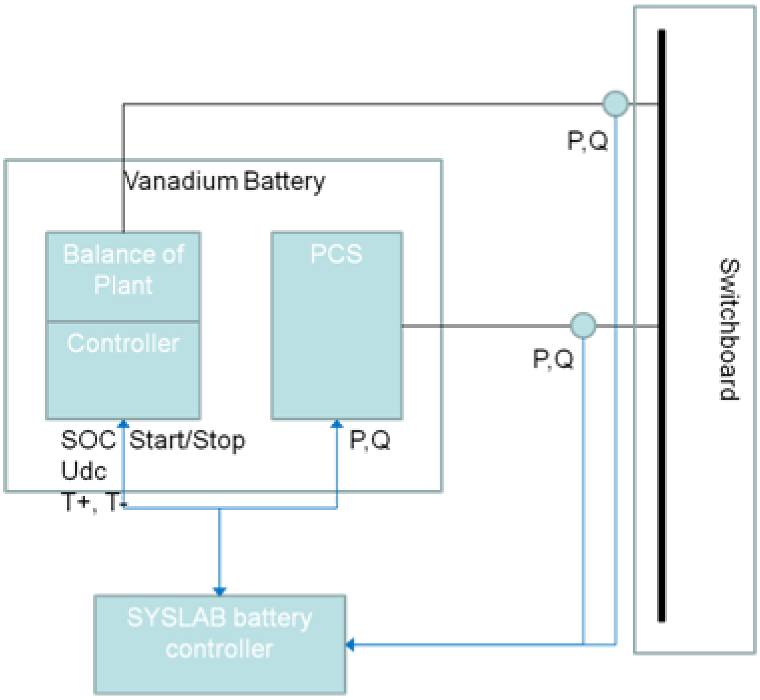

Figure 5 Measurement setup for vanadium battery in SYSLAB

The battery is controlled using dedicated analog signals for active and reactive power in order to secure minimization of the response time.

A graphical control panel for the battery has been developed for interactive control of the battery and a number of controllers have been implemented for various test purposes.

2.4. Operation of the battery in 2008-2009

The battery was installed in August 2007. It operated for three weeks before it experienced a short circuit to ground in one of the cell stacks. A new set of stacks were installed at the end of January 2009. The battery has been operated constantly from February 2008 to August 2009. The stacks then started to leak and operation was suspended. A third set of stacks were installed in November 2009. Data for stacks set II and III have been logged and used to understand the characteristics of the battery. Figure 6 shows the state of charge[1] (SOC) of the battery as function of time during the period of operation of cell stack set II.

1 The definition of state of charge is described in more detail in section 3.2.1. The SOC used in most parts of the report refers to per cent of total capacity as reported by the battery controller.

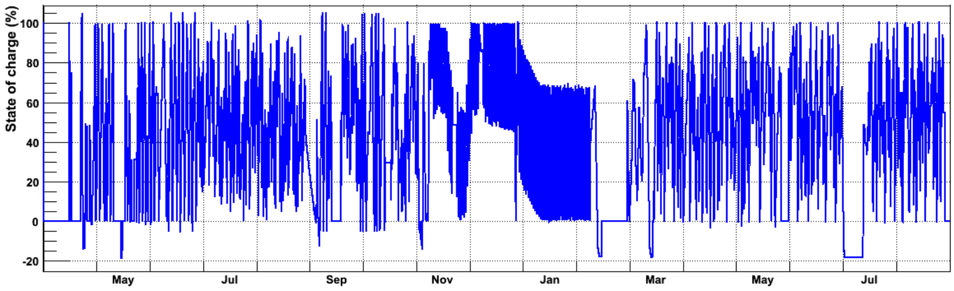

Figure 6 State of Charge as function of time (from April 2008 to August 2009).

Several different operating schedules and test sequences have been applied over the test period of the battery.

- A scan through all power levels from (-15kW to 15kW with 5kW steps) at different SOCs (from 0% to 100% with 5% steps) has been carried out regularly in order to evaluate the battery performance and degradation over time.
- In longer periods, over the spring and summer of 2008, the battery has been set to subsequently charge fully and discharge fully at different power levels.
- During an 11 day period in March 2009, the battery has been set to balance the output from the 11kW Gaia wind turbine, so that the total output to the grid was a constant 4kW.
- During periods in November 2009 and January 2010, alternative controller of the battery has been set to smooth the output from the 55kW Bonus wind turbine.
- During the period from November 2008 to February 2009, the battery has been set to charge and discharge at fixed daily patterns, charging at night and discharging during the day with the maximum discharge power during peak demand hours.
- During the remaining time the battery has been set to charge and discharge to a random SOC with a random power (excluding the periods with other operation modes described above).

3 Characteristics of the Vanadium Battery

The objective of the project is to get hands-on experience with the vanadium battery technology and through measurements characterize the battery as a component in the power system in order to be able to evaluate the performance of a prospective battery in the Danish power system. The characteristics of the battery of interest for the power system are divided in the following headlines

- Efficiency
- Capacity and SOC
- Degradation (Lifetime)
- Operating characteristics

Initially are the losses of the different parts of the battery determined, 3.1. Then the starting and stopping sequence of the battery, the response time and the degradation are described in subsections 3.3, 3.4 and 3.5, respectively.

3.1. Efficiency

Figure 7 shows a schematic picture of the sources of losses of the battery system. In this depiction, the system has four parts: the power converter, the cell stacks, the storage and the auxiliaries. The following four subsections will describe the characteristics of these four parts.

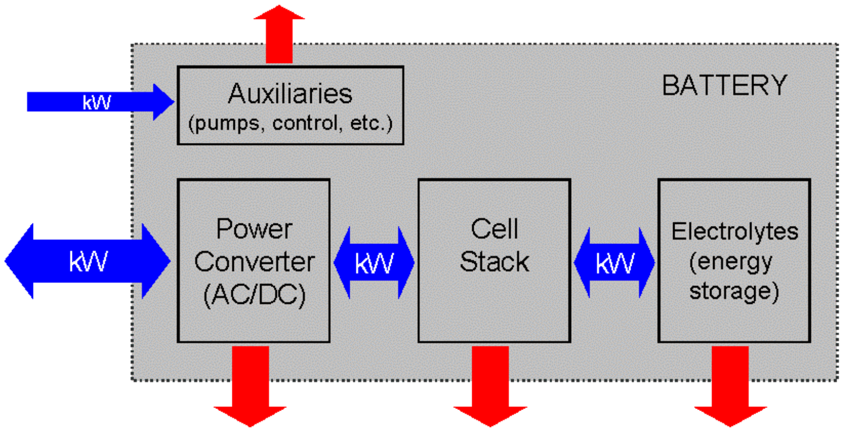

Figure 7 Schematic drawing of the battery system. The red arrows indicate losses from the different parts of the system. These are described in details in subsections 3.1.1 to 3.1.4.

3.1.1 Power converter efficiency

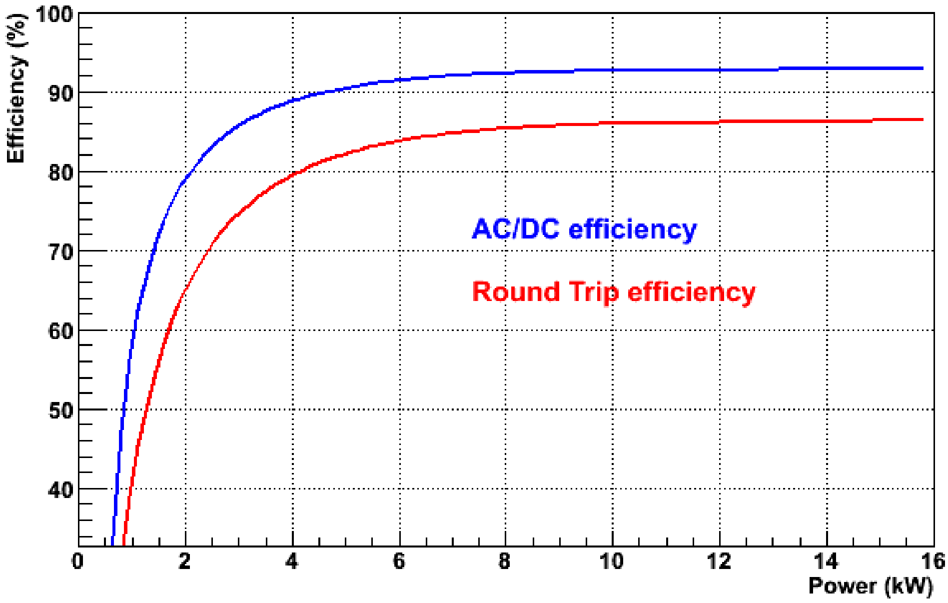

Figure 8 Power converter efficiency as function of power (AC). The AC to DC efficiency and DC to AC efficiency are identical (blue line) and about 93% at full power.

The power converter efficiency has been estimated from the measured power on both the AC and the DC side. The AC to DC efficiency and DC to AC efficiency are identical. The efficiency is shown on Figure 8. At maximum power it is approximately 93% and has a relative large range where it is flat. The absolute efficiency is not very high for a modern power converter.

3.1.2 Cell stacks efficiency

There are three cell stacks with 40 cells in each stack. The stacks are electrically connected in series, which gives a potential of about 165 V. The total cell area is about 1.8×10^5 cm^2 (the area has been measured by hand with a ruler and is not very exact).

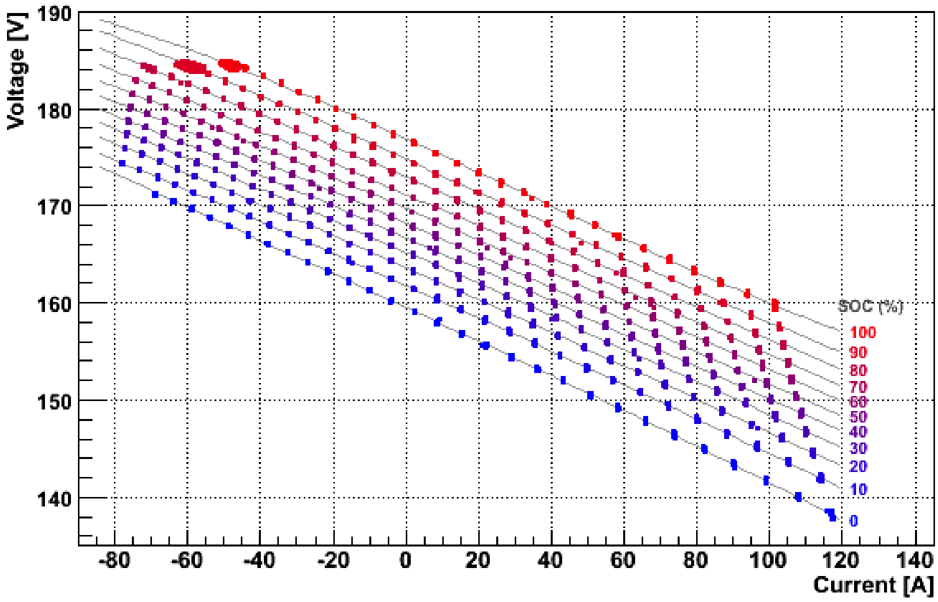

Figure 9 Voltage (over all cells) as function of the drawn current. The different colors indicate the different SOCs. The plot also shows the voltage limit of about 185V. The power is thus limited when charging at high SOC.

The main contribution to losses in the electrochemical cells is the Ohmic resistance (for more details, see ref [Atkins 1987]). Figure 9 shows the voltage as function of the current (i-v curves) over all the cells at different SOC (stable running conditions). The internal resistance is the slope of these polarization curves – it is approximately 0.16Ω. The internal resistance is dominated by the Ohmic resistance and the curves are therefore approximately linear. The small deviation from the linear dependence comes from other minor losses in the cells (these have not been studied). Note also, that the DC-voltage is limited to approximately 185Volts to protect components in the power converter. The voltage limit means that in charge mode, the power (input) of the battery is limited. E.g. at SOC=90% the power is limited to approximately 11 kW.

The power delivered to the stack is $P=V_{DC}\times I$, while the power delivered to the electrolytes is $P = V_{EMF}\times I$. This means that the stack efficiency is V_{EMF}/ V_{DC} in charge mode (when I<0) and V_{DC}/V_{EMF} in discharge mode (when I>0). Figure 10 shows the efficiency of the cell stacks as function of DC power at different SOC levels, when the battery is running in stable conditions. The figure illustrates how the relative deviation from the EMF grows with the power, leading to a decrease in the cell stack efficiency. There should also be a slight efficiency dependence on temperature, but this is expected to be insignificant in the temperature range that the battery is operated in and it has been disregarded in this study.

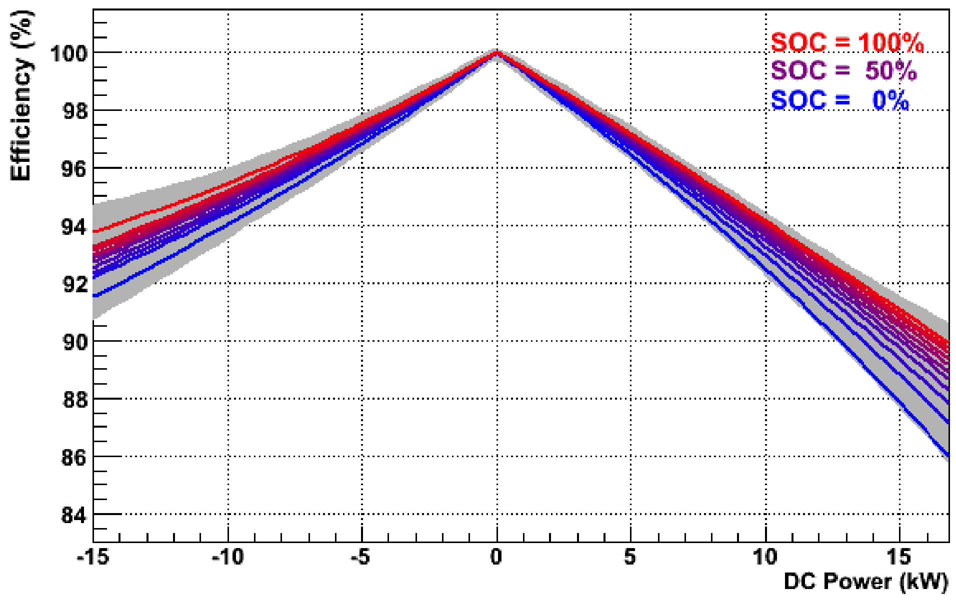

Figure 10 Efficiency of the cell stacks as function of DC power. The different colors indicate the different SOCs. The grey area indicates the variations in the efficiency.

3.1.3 Other storage losses

As a part of the normal operation of the battery, water will diffuse though the cell membranes when the ionic composition in the two electrolytes differs (due to the osmotic pressure). This results in a difference in the level of the electrolyte in the two tanks. In order to avoid a too large difference in the level an equalization process is carried out every 24 hours. A valve between the two tanks is simply opened for about half an hour allowing electrolyte to flow from the tank with the highest electrolyte level to one with the lowest level. The energy loss during equalization depends on the current SOC and of course the difference in electrolyte level. The loss has been measured to be 1.5% SOC (2.7kWh) on average during the measurement period. This corresponds to a constant energy use of about 110 Watts. The losses during equalization are the only observed energy losses in the electrolyte.

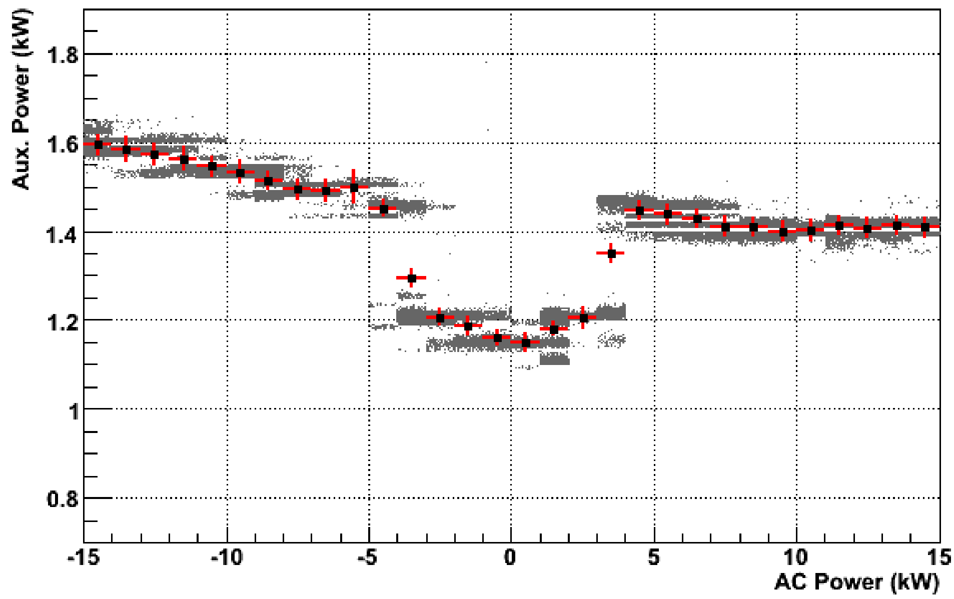

Figure 11 Auxiliary power as function of AC power. The grey regions show data (5 second averages) taken when operating the battery half an hour on each integer AC power (from -15 to 15kW). The red crosses indicate the average value.

3.1.4 Auxiliary power consumption

For a vanadium battery the auxiliary power consumption is significant since the electrolyte has to be circulated for the battery to be operational. The power of the auxiliaries (control system, pumps, etc.) can be derived from the measured AC power of the battery and the total power flow over the bus (when only the battery is connected). When the battery is off, the power consumption (for the control PC and the displays) is 235W. When the battery is on and the pumps are running the power consumption is between 1.1 and 1.6kW depending on the AC power. This is illustrated on Figure 11. At low power ($|P_{AC}|<4$kW) a high flow speed of the electrolyte is not required and the pumps speed is reduced, which can be seen in the auxiliary power consumption. At high power ($|P_{AC}|>4$kW), the pumps are running at higher speed and the auxiliary power is about 1.5kW. The slight AC power dependence observed in the charge mode (and why a similar dependence is not observed in the discharge mode) has not been understood. The fraction of the auxiliary losses will probably decrease with size of the battery e.g. by introducing stages in the battery so only stages that are necessary are in operation. Further might the control of the pumps be more sophisticated and depend more on the current operating conditions.

3.1.5 Overall efficiency

Figure 12 shows the battery efficiency as function of the power (when the power is negative the system is charging). The stack efficiency is highest at low power, but power converter efficiency and the auxiliary power use makes the system efficiency very low (<50%) at low power (<3kW).

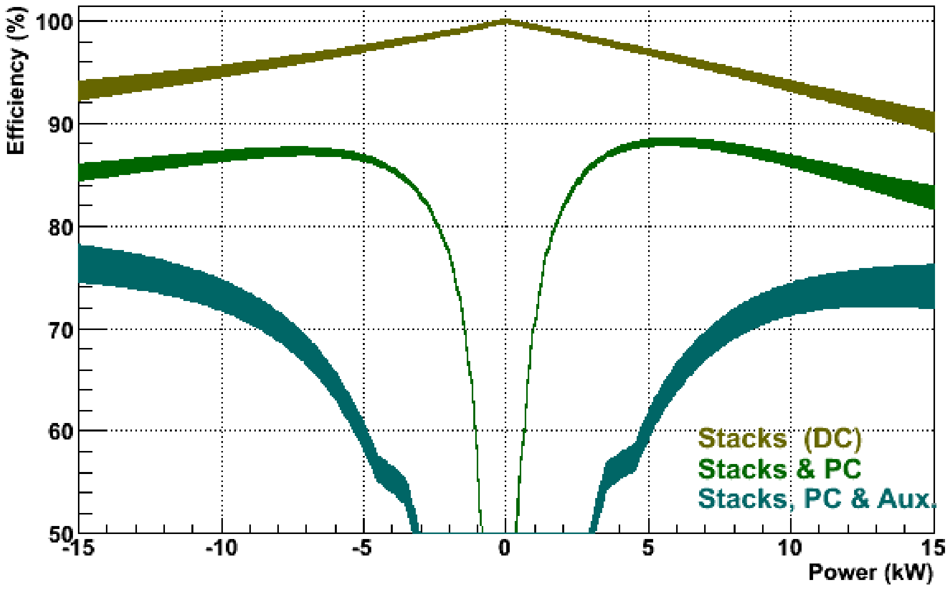

Figure 12 Efficiency as function of power (negative power means charging the battery). The upper (yellow) curve shows the cell stack efficiency as function of power. The middle (green) curve shows the combined efficiency of the cell stack and the power converter. The lower (cyan) curve shows the full efficiency including losses in the equalization process (see section 3.1.3) and auxiliary power. The small "shoulders" around ±4kW comes from the fact that the auxiliary power is lower at low power (see section 3.1.4).

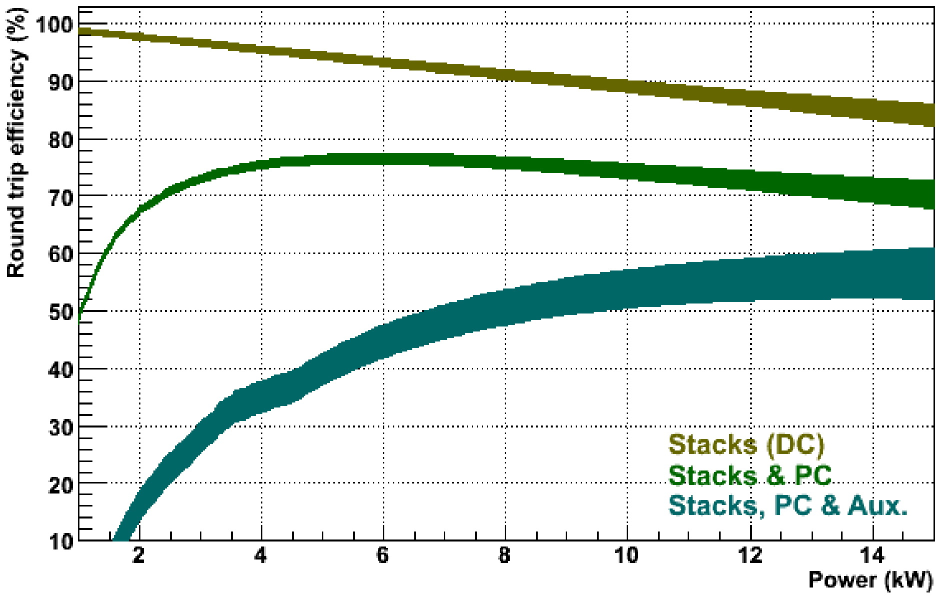

Figure 13 Round trip efficiency as function of power. The upper (yellow) curve shows the round trip efficiency of the cell stacks. The middle (green) curve shows the combined round trip efficiency of the cell stacks and the power converter. The lower (cyan) curve shows the full efficiency.

The round trip efficiency is shown in Figure 13. The system round trip efficiency of around 60% at maximum power could probably be improved by installing less power consuming pump and control system power. There is also room for improvement of the power converter efficiency, but it could lead to an increase in price. It is not expected that the cell stack efficiency can/will be improved significantly.

3.2. Storage Capacity and State of Charge

The following subsections describe how the state of charge (SOC) is determined, how the total storage capacity of the installed system is estimated.

3.2.1 State of Charge

The state of charge (SOC) is a measure of the amount of stored energy relative to the total energy storage capacity of the battery. Two definitions of SOC are used in the current context. One SOC relates to the possible electrochemical energy storage capacity of the electrolyte and the other SOC is the range that the battery controller allows to be utilized during operation. The first SOC is related to the concentrations of vanadium ions in the two electrolytes and it can be determined from the electromotoric force (V_{EMF}) over the cells. A (single) reference cell is installed in parallel to the cell stacks in order to provide a measurement of the V_{EMF}. The electromotoric force is given by

$$V_{EMF} = E_0 + \frac{RT}{2F} \ln\left(\frac{SOC^3}{(1-SOC)^2}\right) \qquad (0.1)$$

where E_0 is standard electromotoric force, R is the gas constant, T is the temperature and F is the Faraday constant. For further details, see Appendix A.

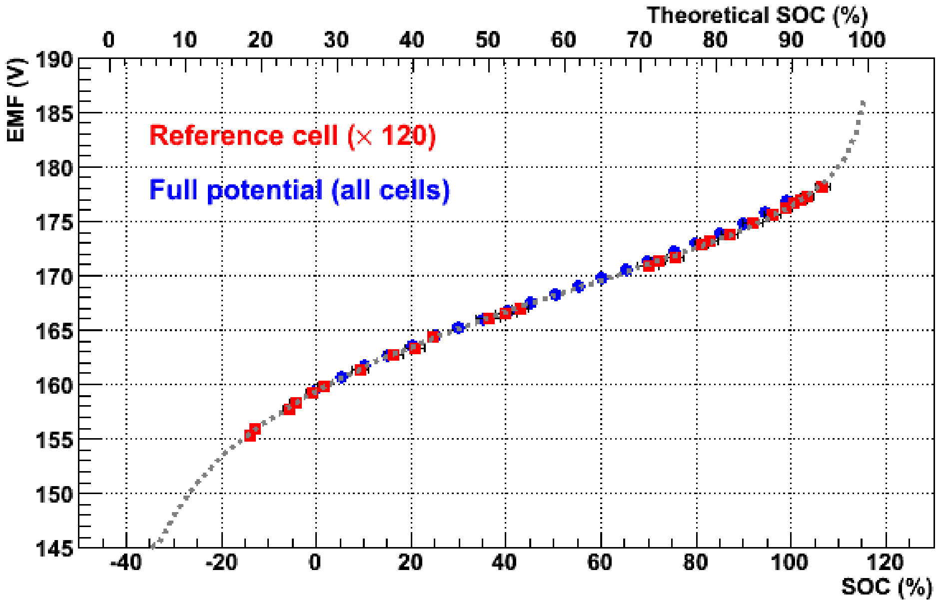

Figure 14 Electromotoric force as function of SOC. The horizontal axis on the lower edge of the plot shows the quoted SOC, while the axis on the upper edge shows the theoretical SOC (for details, see Appendix A). The dotted line shows a fit to the data points (from which the theoretical SOC has been determined).

Figure 14 shows the open circuit voltage (V_{EMF}) as function of the SOC. The axis on the upper edge of the plot shows the theoretical state of charge (see Appendix A). The dotted curve shows a fit to the data points. Due to the resolution of the measurement of the reference cell (V_{EMF}) measurement the SOC fluctuates 2-3%. The SOC used in most of the analysis presented here is the average over 60 consecutive SOC measurements (one each second).

3.2.2 Storage Capacity

The total chemical energy storage capacity can be estimated by ramping the battery from SOC=0% to SOC=100% (or vice versa) and adding the energy delivered to the electrolytes, i.e. the DC current times the open cell voltage (at the present SOC). Figure

15 shows the SOC and the estimated energy stored during such a full ramp. The estimated energy storage capacity is around 180 kWh. This amount is the chemical energy stored in the electrolyte, about 160kWh can then be extracted due the electrochemical conversion losses.

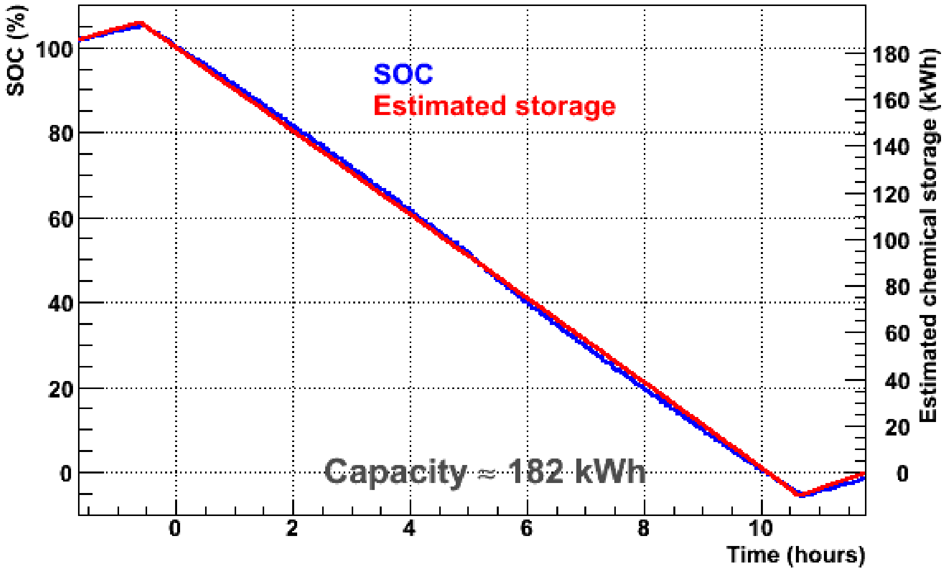

Figure 15 The blue curve shows the SOC as function of time during a full discharge from SOC=100% to SOC=0%. The red curve (right axis) is the estimated chemical energy storage of the battery.

3.3. Starting and stopping

When the battery is not in operation the cell stacks are drained to reduce self-discharge. The start and stop sequences of the battery takes about 7 minutes. During startup the pumps are ramped up in speed and the system is flooded. The flooding period ensures that the stacks are completely flooded. The stop sequence stops the pumps and the electrolyte is drained by gravity (this is the reason for the layout of the system). Figure 16 illustrate a start sequence. The energy consumed during start and stop is less than 0.1 kWh.

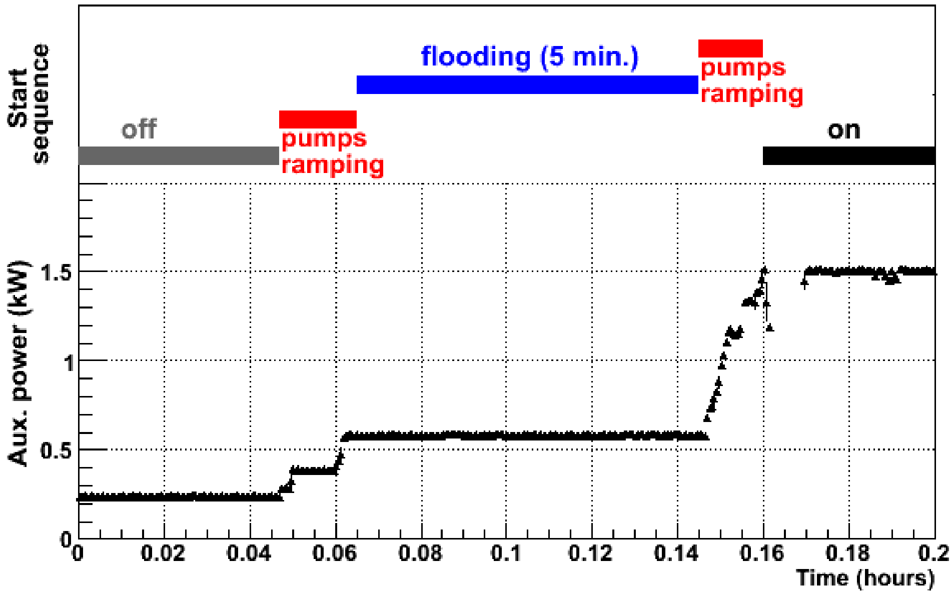

Figure 16 Start sequence of the battery. The lower graph shows the auxiliary power as function of time. While the battery is off the control system still uses about 235W. The power increases to 580W when the system is flooding or draining and further to about 1.5kW when the system is on and the pumps are running at full power.

3.4. Response time and transients

The response time of the battery system is fast compared to other generators in the power system, ensuring that the battery can be used in frequency support of the system. The responses to a positive and a negative step change in the active power setpoint are shown in Figure 17 and Figure 18.

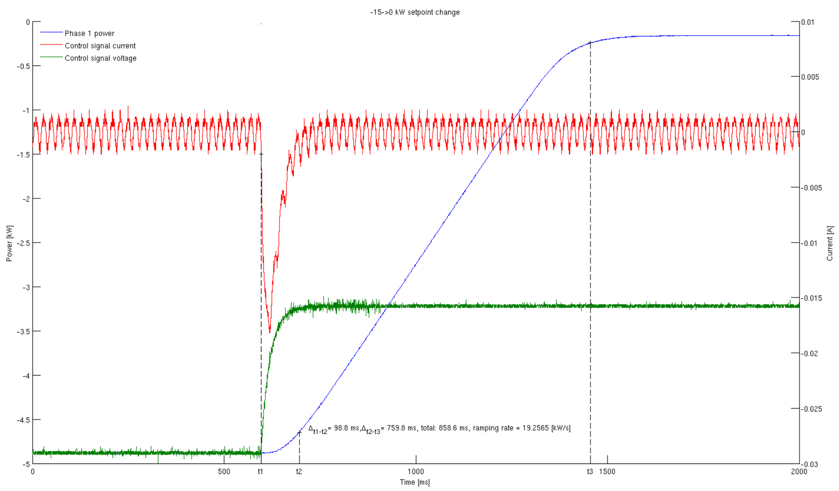

Figure 17 Response to a positive step in active power

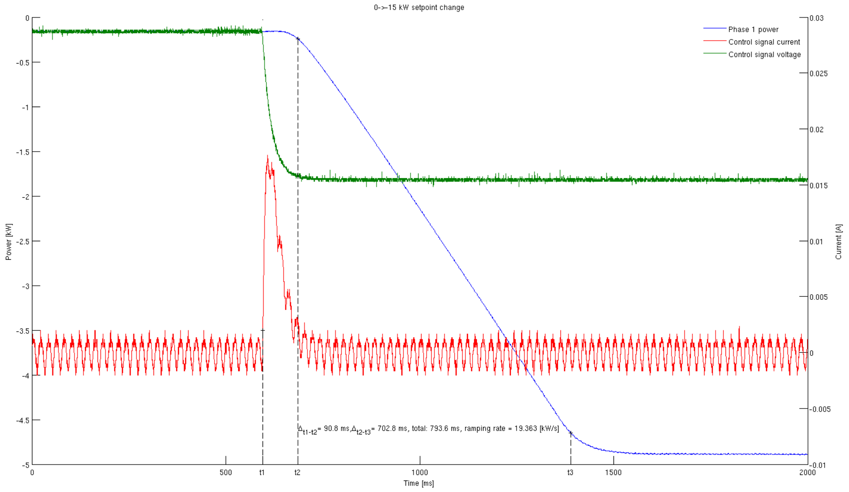

Figure 18 Response to a negative step in active power

The two figures clearly illustrates that the response time of the battery in the present configuration is limited by the ramp rate of the power electronics which is set at 20kW/s. However, this response time is fast enough for the majority of the functions of a battery in the power system and definitely fast enough for delivering frequency support.

3.5. Degradation

Degradation of the battery stacks has been studied by measuring the development of the internal resistance over time (or over energy that has passed through the stacks). The internal resistance is given by the deviation of the voltage from the open cell voltage divided by the current $(V_{EMF} - V_{DC})/I$. The internal resistance is primarily due to Ohmic resistance in the cells while activation losses and other effects play a minor role. The resistance can also change by a few percent with the changes in temperature. In general, the resistance is expected to increase as the cells degrade, leading to lower efficiencies.

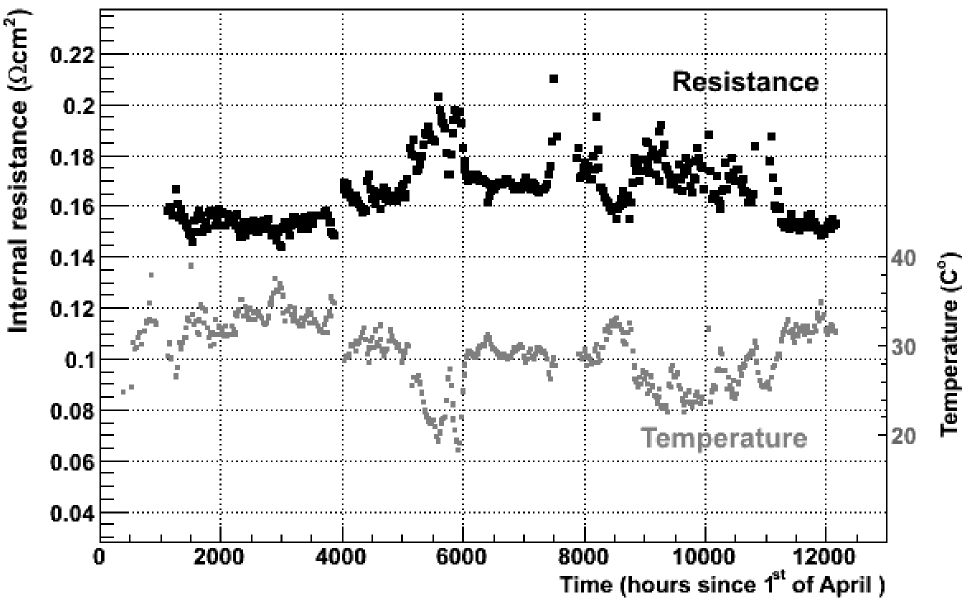

Figure 19 Internal resistance and electrolyte temperature (right axis) as function of time (daily averages). The resistance depends on the temperature, but it increases insignificantly over time.

Figure 19 shows the resistance (and electrolyte temperature, right axis) as function of time. While the resistance is clearly anti-correlated with temperature it does not seem to increase over the 17 months of operation. The temperature dependence has been subtracted assuming a second order correlation between temperature and internal resistance and the result shows no increase in resistance.

3.6. Performance of new set of cell stacks

During the time of the project the technology has been further developed. The main focus of the development has been on maturing the cell technology to lower the manufacturing costs. As the second set of stacks had to be replaced a new set of the next generation was installed. The new set is of a new generation of the stack technology and has two more cells in each stack. The voltage limit of the power electronics was adjusted accordingly. However, the upper dc-voltage limit had to be further increased due to the new cells having a slightly higher internal resistance. The measurements are shown in the next figures.

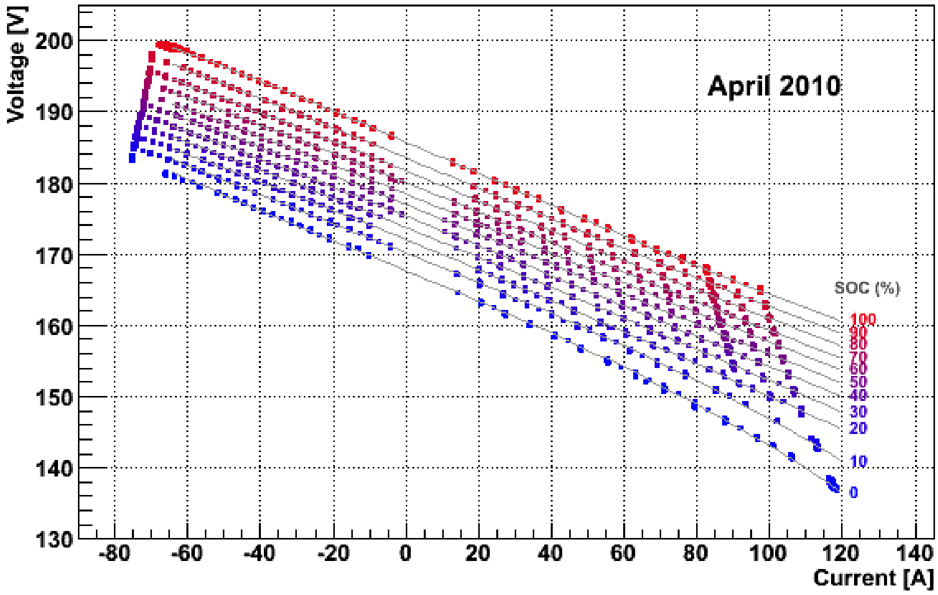

Figure 20 New cell stacks: Voltage (over all cells) as function of the output current. The different colors indicate the different SOCs.

The i-v curves for the new stacks are in Figure 20. The increased voltage span is clearly seen compared to Figure 9. This corresponds to a lower efficiency. The efficiency of the new stacks is in Figure 21 and it is compared to the old stacks in Figure 22. It is clearly seen that the efficiency is lower and that it is due to a higher internal resistance.

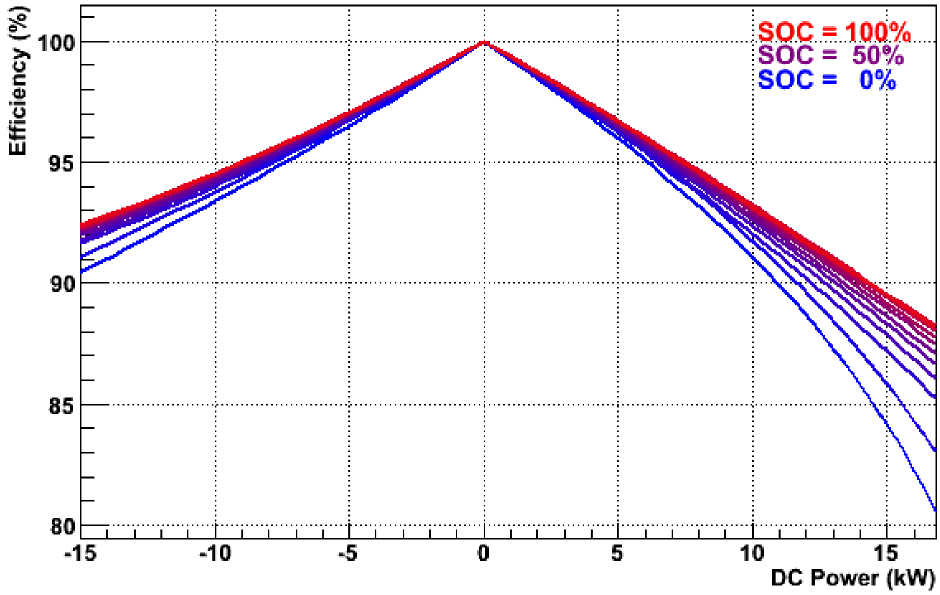

Figure 21 New Cell stacks: Efficiency of the cell stacks as function of DC power. The different colors indicate the different SOCs. The grey area indicates the variations in the efficiency.

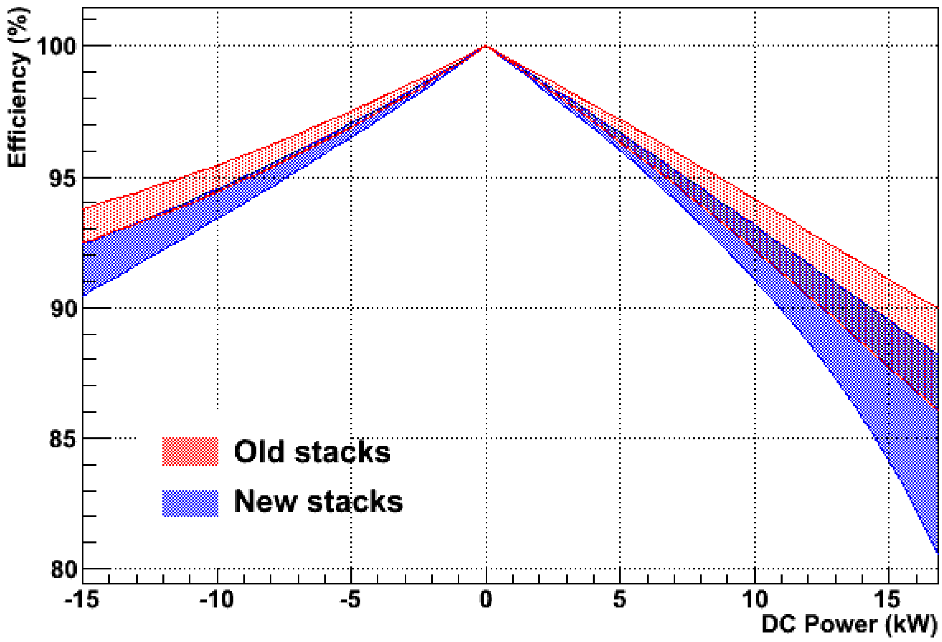

Figure 22 Comparison of efficiency of the two set of cell stacks as function of DC power.

The new stack design is significantly more mechanically robust due to interlocking of the cells and it should also be more suitable for mass production and automatic assembly of stacks, but has a lower efficiency.

3.7. Summary of vanadium battery characterization

In the previous subsection, the analyses of the battery have been described and interpreted. The basic results can be summarized:

- System operation: The battery has been operated almost continuously since May 2008. There has been no need for maintenance and the battery has at any time delivered the requested power.
- Efficiency: The stack efficiency is high (>85%) and the system efficiency is slightly lower due to the efficiency of the power converter, the equalization process and the auxiliary power consumption. The round trip efficiency is about 60% when operating at high power.
- Storage: The chemical storage capacity is around 180kWh (from 0 to 100% SOC), which makes it possible to extract approximately 135kWh from the fully charged battery. This corresponds to 9 hours of discharge at full power.
- Degradation: The degradation of the systems is very small. Over the 17 months of operation, the internal resistance of the battery has not increased.

4 Future Perspectives of the technology

4.1. Technology improvements

The installed and tested battery is an advanced prototype where emphasis by the supplier has been to ensure that the system would be operating robustly. However, the measurement results and the operational experience have indicated a number of potential areas of improvement of the technology. The technology improvements can be divided in three groups:

1. The battery itself, primarily stacks and pumping operation
2. Power converter/grid interface
3. Battery system functions

For the cells stacks the main lines of development are improvement of the expected lifetime of the stacks and improvement of reliability. This is already central to the current R&D activities at the manufacturers, but further improvements are essential and documentation of the performance will be crucial.

The efficiency of the stacks can also be improved, but as is seen with the new set of stacks is not necessarily an objective in itself since it could be more economic to reduce the overall cost of the stacks rather than improve efficiency. The efficiency of the stacks depends on the current density that the stacks are operated at. This means that operating the stacks at low current densities results in high efficiencies, but requires large electrode and membrane area which means more expensive stacks. Presently, the development effort is primarily on lowering the manufacturing costs e.g. avoiding hand assembly as much as possible and secondly improve efficiency.

As is already indicated in the previous sections the testing of the battery has indicated a number of areas where the battery can be improved primarily from an efficiency point of view. The circulation of the electrolyte is done in a very conservative way making sure that there is always enough electrolyte available for the required reaction. It is, however, clear from the measurements that the pumping is responsible for a large fraction of the standing losses of the system and since these losses are occurring as soon as the battery is in operation it is important that they are minimized. Making the pumping rate dependent on the load of the battery will reduce these losses. For large installations the battery could be segmented and only the required segments would be online thus eliminating part of the pumping loss.

The equalization of the electrolyte level should be done on a need basis rather than by a time and further could be done in periods where the SOC is low to reduce the amount of energy that released with flow of the electrolyte.

The power converter efficiency can be improved compared to the installed unit. The performance of the power converter is otherwise good.

A key improvement of the technology is development of functionality that can value to the unit so that it can perform in the power system. This means development of controllers that enable the battery to take on the roles mentioned below in section 5.1 and integrate in the SCADA system.

There are a few manufacturers of vanadium batteries, Prudent Energy energy, Cellennium, Cellstrom, developing slightly different types of batteries and it can be expected that as the market of electricity storage develops these companies will improve the technology.

5 Applications and Alternative Technologies

Electricity storage can take different roles in the power system. These roles range from improving the overall operation of the system to directly mitigate the impact of a particular installation of renewable energy. Further, vanadium batteries are not the only battery solution or even electricity storage technology available.

5.1. Role of Vanadium Flow Batteries in the Power System

Energy storage systems can have many different roles in the power system. The suitability of the different energy storage technologies for a particular application depends very on the characteristics of the technology. This is of course one of the main drivers for the current project.

Internationally there has been has been many projects involving analysis of the functions of energy storage in large power systems and its associated value as well as the suitability and cost of various storage technologies.

One of the most comprehensive studies has been carried out by EPRI and DOE in the USA and the results have been published in the reports [1] and [2]. The reports are published in 2003 and 2004 so they are fairly recent.

In the reports are several applications of energy storage defined as seen below: (the terms used are based in US power system operation)

General Energy Storage Applications

- Grid stabilization
    - Angular stability
      Mitigation of frequency oscillations in the range of a few seconds
    - Voltage stability
      Provide voltage support by injecting both active and reactive power
    - Frequency excursion suppression
      Frequency support by droop control
- Grid operational support
    - Regulation control
      Frequency regulation in concert with load following in the 10 minute range with 10min notice
    - Conventional spinning reserve
      Reserve power for at least 2hour duration at 10min notice
- Distribution Power Quality
    - Short Duration PQ
      Voltage distortion mitigation
    - Long duration PQ
      Voltage distortion mitigation combined with several hours of reserve power.
- Load-shifting
    - Short duration load shifting
      3hour load shift

  - Long duration load shifting
    10hours load shift

Wind specific applications

- Transmission curtailment
  Limiting output from wind farm combined with storage to transmission capacity
- Time-shifting
  Shifting wind power from off peak hours to peak hours
- Forecast hedge
  Mitigating forecast errors
- Grid-frequency support
  Large event immediate spinning reserve
- Fluctuation suppression
  Output smoothing from wind farm

In a Danish context it is of special interest how energy storage can be used to mitigate some of the impacts of integrating large amounts of wind energy. The three applications of primary interest are therefore Forecast hedge, Grid frequency support and Fluctuation suppression.

One of the key elements to increase the wind penetration level is to mitigate the impact of the large and rapid changes to the output of large wind farms that has already been observed at Horns Rev I. These events can happen when the wind speed goes above the cut-out wind speed of the wind turbines or when a front is passing. These events are some of the critical events for the power system as large off shore wind farms are being built and put into operation.

A function that is not mentioned in the US study is the ability to black start the grid. This can also be a valuable function of an energy storage system.
In Denmark transmission curtailment will probably not be relevant since the grid connections of the wind farms as well as the transmission system are/will be sized for the expected very high penetration of wind.

In Denmark ESS could also play a significant role in general grid support as the role of the large central power plants is being reduced due to the increasing penetration of wind and therefore lower energy demand from large plants.

Forecast hedging is very much an economical issue for the owner of the wind farm/seller of wind energy. The ability to better predict the production from wind farms will increase the value of the energy on the market and can thus lead to higher penetration. The role of ESS will depend on ownership, cost of the ESS, value of the services it can provide and if it required e.g. according to grid codes.

5.2. Alternative Technologies

A number of electricity storage technologies can compete with VRB technologies for a number of different applications. This section summarizes these different technologies. Important parameters for electricity storage are the range of power and storage capacity, the response time, system lifetime, self discharge time, system size, operation and maintenance cost and system cost (which in some cases can be split into the power related costs and the storage capacity related costs). It is difficult (or impossible) to obtain certain quantitative numbers for these parameters for any of the technologies. The following gives a brief overview, while more detailed descriptions including estimates for the different parameters can be found elsewhere [1][2][3].

Pumped hydro: Pumped hydro is the most common technology for large scale electricity storage with more than 90GW installed worlds wide. The relatively low costs for the storage capacity makes it suitable for large scale energy management, shifting the demand and supply by hours, days or weeks. The response time of hydro turbines is typically on the order of minutes and the technology is therefore not suited for primary reserves. Construction of pumped hydro systems is limited to regions with the appropriate topology (mountains). However, artificial reservoirs underground can also be used, making it possible to construct pumped hydro systems in places like Denmark. Underground pumped hydro is, due to the excavation of the reservoir, expensive compared to conventional pumped hydro.

Compressed Air Energy Storage (CAES): In CAES systems the energy is stored mechanically by compressing air. In the most common designs, air from the atmosphere is compressed and stored in large storing volumes (typically underground) for later expansion, which generates power via a turbine. The large pressure gradients in the compression and expansion stages leads to undesirable heating and cooling of the air, which is dealt with by intercoolers and heat recuperators. Two large CAES systems have been constructed and have been operated for many years [4]. In both of these systems the generating turbines are using both natural gas and the expanding air of the storage caverns. By doing this, the expanding air gets heated by the gas combustion and the problems arising from the large temperature drop is avoided. The efficiency of the energy storage is not trivial to disentangle from the efficiency of the natural gas combustion. The response time of CAES systems is relatively fast, comparable to that of gas turbines (i.e. suitable for frequency controlled reserves).

Large Scale batteries: A number of other large scale battery technologies have been developed and tested. Most common are the Sodium Sulfur and the Lead Acid batteries, which have been installed in a number of MW scale projects around the world. At this stage these technologies are more mature than the Vanadium battery technology, which means that the costs of the battery systems are lower. However, these sodium sulphur and lead acid batteries suffer from memory effects and relatively short lifetimes (depending on the operation conditions). In general, large scale batteries are suited for frequency controlled reserves, due to their very fast response time, but less suited for energy management (long term storage of large amounts of energy), due to the relatively high cost of the storage capacity.

Electrolysis-Fuel cells: Electricity storage in the form of hydrogen is done by water splitting (electrolysis), hydrogen storage and subsequent conversion back to electricity via a fuel cell (or an internal combustion engine). There are different technologies for both electrolysis and fuel cells and they are used in various applications. However, the market penetration is still very limited. Several projects demonstrating electricity storage (using electrolysis, hydrogen storage and fuel cells) have been set up. The technology suffers from relatively low round trip efficiency and high costs. It seems unlikely that this technology will be able to compete (in terms of costs and round trip efficiency) with vanadium battery technology in any foreseeable future.

Vehicle-to-grid: A large number of grid connected electric vehicles could also be used for large scale energy storage (balance and reserves), if the required communication infrastructure and control is in place. Only about 12% of cars are actually on the road during rush hours [5], which means that a very large fraction of the electric vehicles could function as energy buffer many hours every day. This concept naturally depends on the future size of the electric vehicle fleet. The round trip efficiency of the batteries in electric vehicles is expected to be comparable to that of the large scale battery systems (>80%). The costs of the grid electricity storage are difficult to evaluate since this will be a secondary service that the batteries provide. There will however be additional costs related to the necessary fast communication and control.

Other technologies: Other technologies for special application (very high energy density or power density) have been developed, e.g. flywheels, supermagnetic electricity storage and super capacitors. These cannot be regarded as competitors to the vanadium battery technology and are not treated here.

6 Summary

As the fraction of renewable energy increases the challenge of maintaining economic operation also increases in particular the need to handle the short term fluctuations and the stable operation of the grid.

One of the options to handle these issues is use of batteries. Vanadium batteries are of special interest in this context as they from a operational point of view has features that make them well suited for this type of operation. This include the ability to withstand very large number of cycles, independent sizing of power and energy capacity and simplicity to maintain.

In the present to project a vanadium battery of 15kW/120kWh has been installed and tested in SYSLAB at Risø DTU. The project had the objectives to get hand-on experience with the technology, characterize it from a power system perspective and assess the applicability of the technology in a Danish wind power integration context.

The battery has, after installation and initial exchange of cell stacks, operated continuously for 18 months either cycling or in parallel with a wind turbine. During this period the round trip efficiency has been measured to be approximately 60% at full load. One of the main reasons for the rather low efficiency is the nearly constant auxiliary power consumption from pumps and controller that amounts to almost 10% of rated power. The stacks are quite efficient, round trip efficiency above 80% at full load, and power electronics being the last main source of losses.

During the testing period the battery has not shown sign of degradation in the performance do to the usage and operation of the battery.

The response time of the battery is fast and currently limited by the power electronics at 20kW/s. This is fast enough to deliver the ancillary services including frequency support in the Danish power system.

The installed battery is of prototype character designed for robust performance. The operation of the pumps has not been optimized for power consumption but for trouble-free operation and the situation is the same for the power electronics for which the controls has been designed for this application. The three sets of cell stacks have also been quite different showing fast development of the stack technology.

Vanadium battery technology is interesting from a renewable energy perspective and has potential for be a part of the future power system provided the technology is further matured and competitive with other potential technologies offering similar service to the grid.

7 References

[1] EPRI-DOE, Handbook of Energy Storage for Transmission and Distribution Applications, EPRI Palo Alto, CA, and the U.S. Department of Energy, Washington, DC: 2003. 1001834

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Appendix A State of Charge and Cell voltage

The SOC is simply the concentration of V^{5+} (i.e. VO_2^+) relative to total concentration of vanadium (in the positive electrolyte) or the concentration of V^{2+} relative to total concentration of vanadium (in the negative electrolyte). In other words

$$SOC = \frac{[V^{5+}]}{[V]} = \frac{[V^{2+}]}{[V]}$$

The Nernst equation gives the relation between these concentrations and the V_{EMF} (or open cell voltage) on each of the half cells.

Positive half cell: $$V_{pos} = E_0^{pos} + \frac{RT}{F} \ln\left(\frac{[VO_2^+][H^+]^2}{[VO^{2+}]}\right) \quad (0.2)$$

Negative half cell: $$V_{neg} = E_0^{neg} + \frac{RT}{nF} \ln\left(\frac{[V^{2+}]}{[V^{3+}]}\right) \quad (0.3)$$

E_0 is the standard (or equilibrium) electromotoric force, R is the gas constant, T is the temperature and F is Faraday constant. The expressions in the logarithmic functions can be rewritten as functions of SOC and the relation between the SOC and the full V_{EMF} is:

$$V_{EMF} = E_0 + \frac{RT}{F} \ln\left(\frac{½SOC^3}{1-SOC}\right) + \frac{RT}{F} \ln\left(\frac{SOC}{1-SOC}\right) = E_0 + \frac{RT}{2F} \ln\left(\frac{SOC^3}{(1-SOC)^2}\right) \quad (0.4)$$

In order not to reach states of very high charge or very low discharge where undesirable chemical reactions will take place, the battery is only operated in window of the full charge range. The SOC provided by the battery is a linear function of the theoretical state of charge ($SOC = a+b\times SOC_{theory}$). This is depicted in figure ?. When SOC is used elsewhere in this report, it refers to the SOC provided by the battery and not the theoretical or real state of charge.

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